

**The Impact of Ozone-Safe Refrigerants
on Refrigeration Machinery Performance and Operation**

David A. Didion D.Eng., P.E.
National Institute of Standards and Technology
Non-Member

ABSTRACT

The current ozone depletion crisis has impacted the refrigeration and air conditioning industry like no other event in history. The limitations placed on the development of machinery working fluids is causing major design changes in new equipment and modifications to existing equipment that will require owner/operators to face many decisions in what was previously a rather staid purchasing process. The elimination of chlorine from the refrigerants has forced the adoption of ester based lubricants in lieu of mineral oils. Molecular and thermodynamic constraints have brought about the expansion of the use of azeotropic refrigerant mixtures and the introduction of zeotropic refrigerant mixtures, with their variable composition problems. For the first time in many years, flammable refrigerants are being used, at least as minor components in mixtures. The transition period of the next several decades is likely to require the use of "drop-in" replacement fluids which can cause a capacity and/or efficiency change in the machine's performance. Furthermore, all the new alternative refrigerants (i.e., replacements) may themselves be unable to meet future environmental restrictions if the global warming crisis proves to be a political reality.

The chemical and thermodynamic limitations and impact, of the new refrigerants, will be presented. Practical ramifications on the machinery performance will be emphasized in a generic manner. At least one problem unique to marine refrigeration, that of the R-114 replacement, will be discussed with its implications for both new and existing machines. The concept of using refrigerant mixtures will also be discussed with emphasis on the impact they can have on system performance as well as maintenance procedures. Some physical properties of the new lubricants relative to the old oils will be noted. Finally, it will be explained how non-flammable mixtures can become flammable under extreme conditions.

1. INTRODUCTION

The working fluid in a vapor compression refrigeration system must satisfy a number of requirements in order to sustain an efficient, reliable machinery system. These requirements are summarized in Table 1. The most essential characteristic is chemical stability while in the refrigeration system. All other properties would be meaningless if the refrigerant decomposed or reacted to form other chemicals with different operating properties. To the refrigeration engineer, stability has been one of the most attractive features

of the fully halogenated hydrocarbons or chlorofluorocarbons, CFCs e.g., 11, 12, and 502). In fact, they are so stable that once released to the atmosphere, they remain intact in the troposphere long enough to reach the stratosphere (> five years) (Roland, 1993) where their disintegration frees up the halogens (i.e., chlorine and bromine) to react with the ozone layer. Partially halogenated compounds with some hydrogen (HCFCs e.g., 22) have more of a balance in that they also remain stable within the refrigeration system indefinitely (for all practical purposes) but have a much shorter atmospheric life due to the hydrogen atoms.

Table 1. Requirements for a Refrigerant

Necessary	<ul style="list-style-type: none"> - stability - safety (non-flammable, non-toxic, environmentally benign) - thermodynamic properties
Desirable for Machinery Reliability	<ul style="list-style-type: none"> - lubricant solubility - material compatibility - low moisture solubility - transport properties - high dielectric strength
Desirable to Facilitate Application	<ul style="list-style-type: none"> - ease of leak detection - amenable to recycling - ease of handling - recharging - low cost

The reason CFCs and HCFCs were developed was to minimize the need for the flammable and toxic refrigerants (e.g., SO₂, NH₃, HCs, etc.). As a result, the refrigeration industry has developed one of the safest product lines in our society, today. To reverse this direction, by using even mildly flammable and/or toxic fluids, is something the U.S. Industry is resisting most strenuously. In a society of litigation mania, having machines containing such fluids within the proximity of the general public, along with relatively poorly trained maintenance technicians, exposes the manufacturers to a higher level of risk than they currently have. Thus, their desire to maintain existing safety standards is quite understandable. On the other hand, the new requirements for

environmental compatibility also restrict the choices one has for selecting alternative refrigerants. In 1928, Midgley, the developer of CFCs, showed that only eight elements lend themselves to be used as atoms for a refrigerant molecule (see Table 2) (Midgley, 1937). All other elements either form solids (in the temperature and pressure range of concern) or are toxic or unstable when combined into molecules. Noble gases being an exception, but they tend to have "no chemistry" (i.e., difficult to combine). In 1987, we at NIST did a data review of more than 800 industrial fluids for their potential as refrigerants and found virtually no exceptions to Midgley's conclusions. Now the ozone problem is eliminating the use of two of these eight: chlorine and bromine. When one considers that sulfur is not likely to yield a desirable molecule for toxic reasons and that hydrogen and oxygen can be used only sparingly for flammability reasons, the molecular choices get alarmingly few, even before thermodynamic considerations.

Table 2. Midgley's Elements

Carbon	Hydrogen
Nitrogen	Fluorine
Oxygen	Chlorine*
Sulfur	Bromine*

*United Nations agreed to eliminate use for refrigerants.

The prime environmental consideration from a thermodynamic viewpoint is efficiency or in refrigeration vernacular the machine's or system's Coefficient Of Performance (COP). The point being that if the alternative refrigerant results in an increase in power input to do the same job more fossil fuel will be combusted somewhere and an

increase in atmospheric CO_2 will result. Thus, refrigerants are now characterized by a Total Equivalent Warming Impact (TEWI) factor which is a composite of the direct environmental warming the refrigerant molecule itself will eventually do when it ultimately escapes to the atmosphere and the indirect warming effect by additional CO_2 generated over the life of the system from the efficiency decrease relative to the CFC or HCFC that is being replaced. Figure 1 shows the relative merit of some of the alternatives and systems that have been analyzed (Fairchild, 1991). As might be expected, one can see that alternative refrigerants in systems that contain their initial charge for a long time make the biggest environmental impact through their indirect effect. An extreme example is seen in the replacement of electric driven compression chillers, using CFC-11, by a double-effect absorption system, whose fluids are environmentally benign. The figure shows that more harm is done to the environment over the life of the unit because of the decrease in efficiency. Efficiency, therefore, is as important for environmental reasons as it is for economics.

Virtually all of the current alternative refrigerants under consideration remain partially halogenated hydrocarbons, that is, they contain hydrogen. Figure 2 illustrates schematically the methane and ethane series and the numbering system is explained in Appendix A. Generally speaking, fluids of additional molecular complexity (i.e., partially halogenated propane, butane, etc.) begin to demonstrate increasingly poorer efficiency potential for the vapor compression cycle for basic thermodynamic reasons that are difficult to be overcome by system design. There are a few exceptions to this trend within the propane family (R-200 series), which will be discussed below, not to mention the base hydrocarbons themselves. But in general, there seems to be little hope in finding a satisfactory family of alternatives in complex molecular fluids. As indicated in the triangles, too much hydrogen left on a hydrocarbon molecule (i.e., R-50 methane or R-170 ethane) makes it flammable while no hydrogen makes it environmentally harmful (if it also contains chlorine) because of its long atmospheric life. Refrigerants with too much chlorine have not been used traditionally anyway because of toxicity. Thus, the choices within these molecular families are quite limited, even if mixtures of these fluids are considered.

Under the current international agreements, the chlorine-containing molecules that also contain hydrogen (HCFCs) will not be phased out for another decade or so and, thus, are available as alternatives for at least one more generation of machines. In this paper, as well as in practice for the immediate future, HCFCs will be considered as part of the solution (short term) as well as the problem (long term).

2. THERMODYNAMIC PERFORMANCE

To realize the technical depth to which this problem and solution have penetrated the refrigeration technology, it is useful to briefly consider the basic thermodynamic principles of the vapor compression cycle. Figure 3 shows the ideal vapor compression cycle (a.k.a. reverse Rankine cycle) on a temperature-entropy diagram. Part of the refrigerant is flashed

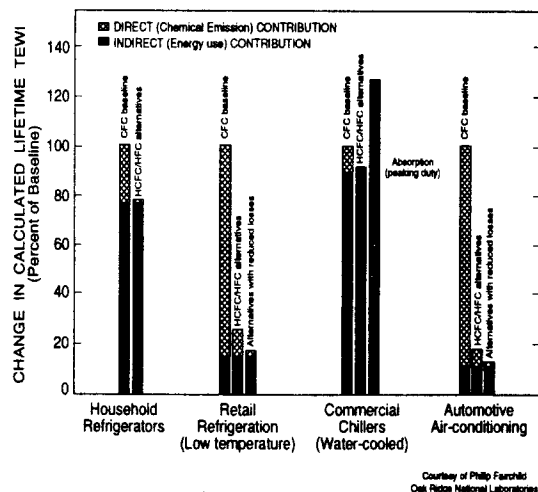


Figure 1. TEWI Values Relative to Baseline CFC Technology

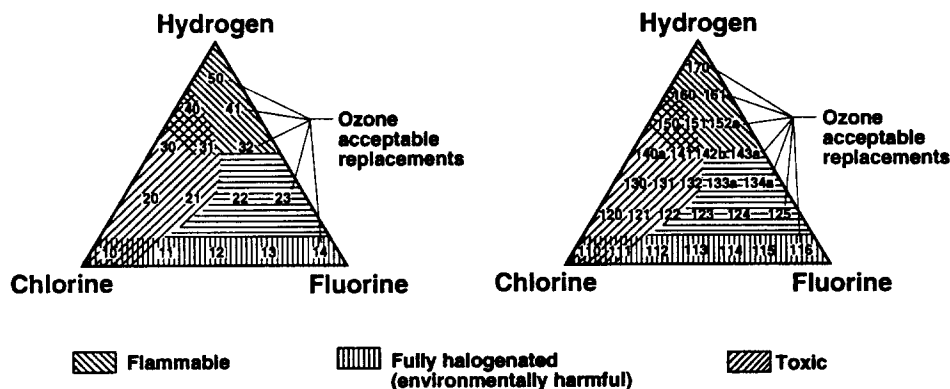


Figure 2. Methane & Ethane Series Refrigerants

while passing through an expansion device (1-2) so the liquid portion is cooled to the desired evaporator temperature. The two-phase fluid then completes its evaporation by drawing

(CP), of the same general shape shown in Figure 3, but of varying widths. Using CP as an index, one can see the consequences that choosing an alternative working fluid are

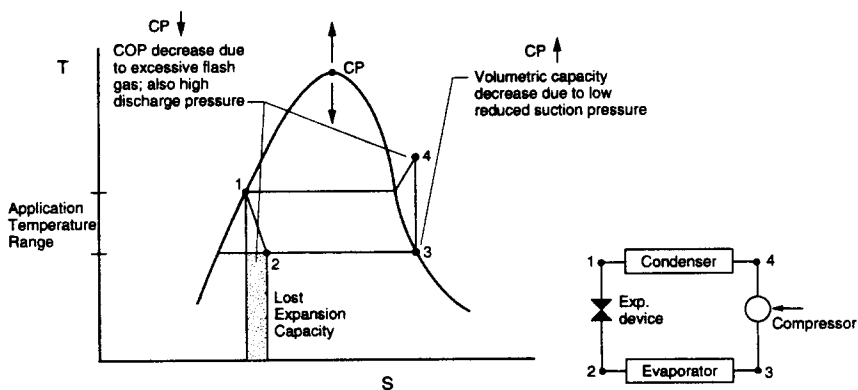


Figure 3. Inherent Trade-offs for Pure Refrigerants

heat through a solid wall heat exchanger from an external fluid (e.g., air or water) on the other side (2-3). The exiting vapor is sucked into the compressor where it is raised in temperature and pressure by mechanical work (3-4). Finally, the discharged vapor is desuperheated and condensed by expelling heat through the heat exchanger walls that are being cooled by another external fluid (e.g., air or water) (4-1). The fundamental trade-off here is that for the purposes of either heating or cooling one of the external fluids, the refrigerant's temperature is raised at the expense of inputted mechanical work. Different refrigerants tend to do this with more or less effectiveness; that is the refrigerant itself can be given an efficiency (COP) value. A higher relative value says, in effect, that a given volume of the refrigerant can transport more heat, through its phase change, per unit power input, than another refrigerant of lower COP value. Although each refrigerant has different numerical values for its various thermodynamic properties (e.g., enthalpy and entropy) all fluids have vapor domes, i.e., saturated liquid (left side) and saturated vapor (right side) lines meeting at the critical point

likely to have on the thermodynamic performance of the refrigeration system. For example, if the only available alternative has a critical point further from the application temperature range, which of course hasn't changed, than the CFC it is replacing, then it might be expected that a lower density suction vapor (mass flow rate) would be entering the same sized constant speed (volume) compressor and so less evaporator heat transfer may occur. Conversely, the selection of an alternative whose critical point is closer to the application temperature range will result in higher refrigerant mass flow but also a higher discharge pressure from the compressor and possibly additional flash gas to cool the liquid returning from the condenser will be required. The net effect is a decrease in COP for fluids of significantly different CPs. Thus, as a general rule, it can be expected that a trade-off between COP and capacity occurs. For retrofit cases where fluids of similar CPs are being considered, the latent heat to liquid heat capacity ratio of the different fluids may dominate the theoretical efficiency value.

Figure 4 illustrates another thermodynamic diagram

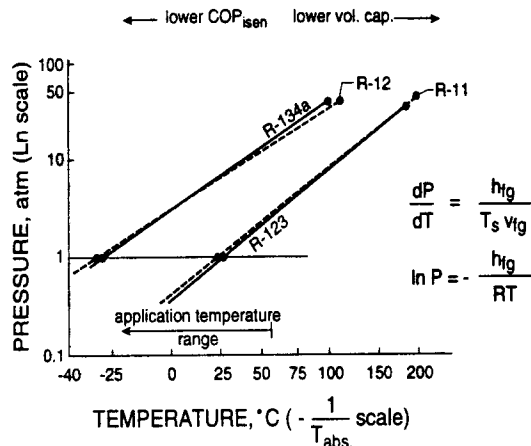


Figure 4. Phase Diagram of CFCs and Alternatives

of the saturation pressure versus temperature on nonlinear coordinates so as to make the plots linear. To the thermodynamist, this is a graphical representation of the classical Clausius-Clapeyron equation but it is also a presentation of the table every technician carries in his pocket to enable him to determine how much refrigerant charge to put in a machine. The four refrigerants shown are two of the most widely used CFCs and their designated alternatives. It was indeed fortunate that alternatives with such similar vapor pressure relationships existed. It means that relatively few machine design changes are necessary to utilize the alternatives and in many instances "drop-in" replacements in existing equipment will be possible, at least thermodynamic-wise. Where the alternative's line is below that of the CFC it can be expected that the capacity would be less or in the case of the new equipment the compressor and/or heat exchangers may be a little larger to obtain the same capacity. Each alternative has a slightly lower theoretical efficiency. However, many of the new machines are being redesigned to make up this difference and then some, because of the need for energy conservation. The CFC-11 and its associated centrifugal compressor water chiller equipment have been the most efficient systems, ideally and practically. This refrigerant's high efficiency low capacity characteristics tend to make it be utilized primarily in flooded evaporator/centrifugal compressor systems. The centrifugal compressor, with its limited compression ratio, further limits it to water chilling (air conditioning) applications. Newly developed HCFC-123 systems are showing similar performance with the potential for improvements through improved machine components. However, as with CFC-11, the sub-atmospheric evaporator pressure has proven to be a limiting factor for marine applications because of the potential of salt air leaking into the system and shortening the compressor life. The medium pressure CFC-12 is widely used

in a variety of applications—from residential, commercial, and industrial refrigeration to automotive air conditioning. From a transition viewpoint, HFC-134a appears to be making the adaptation more broadly than any other alternative. Retrofit to existing CFC-12 systems appear to be possible in many applications.

In 1991, the Shipowners Refrigerated Cargo Research Association (SRCRA) carried out an experimental retrofit of a CFC-12 clip-on container refrigeration unit to HFC-134a. By 1993, the Cambridge Refrigeration Technology (CRT) had completed 10 such retrofits. Heap (1993) has presented a paper of the summary results and experiences. He suggested, theoretically, that with the required low evaporator temperatures (i.e., $< -15^{\circ}\text{C}$) a capacity loss of up to 20% could be expected, due to decrease in suction pressure and increase in pressure ratio of the HFC-134a. This may be confirmed by examining Figure 4. It can be seen that at low temperatures the HFC-134a saturation line is below that of CFC-12 and its slope is steeper. Actual 50 Hz test results showed a capacity loss range of 3 to 21% with a somewhat proportional power loss and even larger losses for 60 Hz tests due to higher pressure losses, inter alia. Details on power measurements were not reported for proprietary reasons. However, system efficiency is seldom increased with such changes because of decrease in the compressor's volumetric efficiency and constant parasitic losses (i.e., fan and/or pump power, compressor friction, etc.). Although in this case, HFC-134a heat transfer coefficients are superior to CFC-12 and improved heat exchanger performance may help mitigate the efficiency decrease. Heap also reported that recent SRCRA work with flooded evaporators, suction accumulator and liquid subcooler tended to improve the HFC-134a performance relative to CFC-12. This tends to support the theory by Domanski and Didion (1992) that refrigerants of higher heat capacity will have improved performance through the use of liquid line/suction line heat exchangers. With continued study, it appears that eventually retrofitting CFC-12 refrigeration shipping containers with HFC-134a will result in acceptable performance for most loads and it represents the preferred option at this time.

Because of the early commitment by many chemical and machinery companies to HFC-134a some new applications are being attempted. One major manufacturer has developed a HFC-134a centrifugal compressor/water chiller with a power turbine in the two-phase expansion side of the cycle to make up for its inherent decrease in the refrigerant efficiency relative to HCFC-123. The same manufacturer is also producing a HFC-134a residential heat pump now, in competition with the higher pressure HCFC-22, long before the HCFC restrictions are scheduled to take effect. This type of innovation suggests that the industry seems to be thinking that: as long as change is inevitable, we might as well try machinery innovations to optimize performance for marketing purposes. It also reflects that society is becoming more energy conservation conscious, as well as the growth of utility rebates programs. Such ventures bode well indeed, for the future of our environment. Even traditional systems appear to be in for performance improvements. Premium models of HCFC-11 chillers are rated at a COP = 5.4 (.65 kw/ton). New

HCFC-123 models are having heat exchangers enlarged and utilize enhanced heat transfer surface tubes to achieve a COP = 6.4 (.55 kw/ton) (Hickman, 1994). One major manufacturer has achieved a COP = 6.8 (.52 kw/ton) with the addition of improved compressor design. This was enabled by the increased head (note Figure 4 the slope of HCFC-123 > slope of CFC-11) of HCFC-123 which allowed the three stage CFC-11 compressor to be changed to two stages for the HCFC-123 (Glaum, 1994). Of course, the heat exchanger improvements will result in increased capital costs so it remains to be seen if the consumers are willing to make the capital investment for life cycle net gain and at the same time carry out their responsibility to the environment.

3. REFRIGERANT MIXTURES

As noted above, the primary approach industry has taken to fill the void resulting from the elimination of the most important CFCs (i.e., 11 and 12) has been to develop other single component refrigerants (123 and 134a) which have very low and zero ozone depletion potential, respectively. These alternatives were attractive mostly because they had similar vapor pressure-temperature profiles relative to the CFC they were replacing. No such single component alternative has been discovered for the higher pressure refrigerants HCFC-22 or CFC-502. As a result, the industry has begun an intensive effort to adopt various mixtures of HCFCs for the short term (see Table A1) and HFCs for the long term (see Table A2), in an attempt to provide a working fluid of a thermodynamic performance equal to or greater than the CFC it is replacing.

For retrofitting existing equipment, a capacity similar to that provided by the CFC is likely to be of prime importance. Capacity is primarily a function of suction density and so the components of the mixture must be adjusted to offer a similar saturation pressure, at the application's evaporator temperature, as previously existed with the CFC it is replacing. The resulting mixture composition may have a lower efficiency, particularly when the flammable components (e.g., HFCs 152a, 32, 143a, 142b, and HCs 290, 600a) must be limited so as not to make the mixture flammable, even under the most severe "fractionation" conditions. Other factors such as compatibility with mineral oil and/or alkylbenzene lubricants also place restrictions on the design of mixtures. For this reason, primarily, the need to use HCFCs has continued for use in alternatives for the transition period (see Table A1). Their chlorine content, albeit minor, is sufficient to allow the use of the lubricants with a long history of reliability and avoids concerns about thorough flushing of old oils or mixing effects with synthetic lubricants. Chlorine-free mixtures are, in some cases, also being proposed as potential retrofit alternatives but for the most part they are intended for newly designed systems. They have benefited from lubricant research (i.e., polyalkylene glycol and polyol esters) that was conducted to meet the needs of HFC-134a. Being totally free of chlorine they meet all of the international restrictions resulting from the ozone problem and are the basis for the new equipment design for applications currently using CFC-12, CFC-502, and HCFC-22.

Refrigerant mixtures in the form of azeotropes (ASHRAE 500 series) have been utilized by the industry for many years. An azeotrope may be defined for practical purposes as a mixture of fluids which has the same composition in the vapor phase and liquid phase, when in equilibrium. Thus, these mixtures will have the liquid and vapor phases at the same temperature throughout the evaporation and condensation processes and are in every way dealt with as though they were single component fluids. Unfortunately, they are quite rare and of all the mixtures listed in Tables A1 and A2 only one has shown azeotropic behavior and that has been rigorously so only at very low temperatures. Nevertheless, azeotrope-like behavior is exhibited by several mixtures which is indicated by small temperature glide (i.e., the difference between the vapor and liquid equilibrium temperatures), such as something less than 1°C. The fact that the different phases are at different temperatures is indicative that the liquid and vapor are of different compositions and herein lies the problem with these zeotropes (a.k.a. nonazeotropes). Since system leaks and recharging often stem from containers where the mixture is in a two-phase equilibrium state (e.g., evaporators, condensers, storage cylinders) the composition will fractionate during phase change making it difficult to know what the new composition is exactly, particularly under field conditions. One solution is to simply recharge with liquid of the original composition and live with the consequences. Such procedures are being now evaluated by the chemical manufacturers. The effect on capacity of a series of leak/recharges is illustrated in Figure 5 for the zeotrope R-32/125/134a (23/25/52% wt.). For either case considered, it would appear that the capacity degradation would tend to level off somewhere in the 90%-of-original range. Alternatively, of course, the balance of any residual charge could be recovered for recycling and a completely new charge of original composition could be installed with no change in capacity. Perhaps for smaller systems (e.g., residential air conditioners) the latter procedure would be preferred. Again, the temperature glide shown is an index as to how severe this phenomena is for a given mixture.

Since HCFC-22 constitutes the largest refrigerant market, by far, the focus of development has been on its alternative. In new commercial equipment, HFC-134a is a strong candidate for replacing HCFC-22. In both commercial and residential unitary equipment two new mixture candidates have emerged in the U.S.A.: HFC-32/125 (50/50) and HFC-32/125/134a (23/25/52). The HFC-32/125, with its azeotrope like behavior, is attractive for its traditional field handling practices; but also for its potential for smaller sized equipment and the possibility of improved COP. However, its vapor pressure lies close to HFC-32 which is considerably higher than HCFC-22, as can be seen in Figure 6. This means that the machinery manufacturers must determine if the economic trade-offs of compressor redesign and higher pressure containment, with its increased wall thicknesses and stronger sealant (i.e., brazing instead of soft solder) requirements, are offset by the small volumetric capacity requirements (i.e., reduced capital costs). It is also thought to be a possibility that the efficiency of such a system could be greater than its HCFC-22 counterpart because the reduced friction and

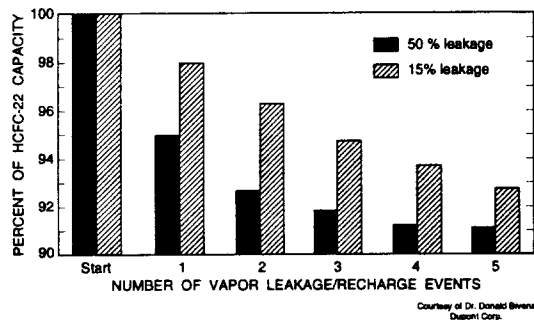


Figure 5. Capacity Degradation with Recharging of R-32/125/134a (23/25/52% wt.) Mixture

pressure losses of the more dense fluid might compensate for the isentropic efficiency decrease this fluid has relative to HCFC-22.

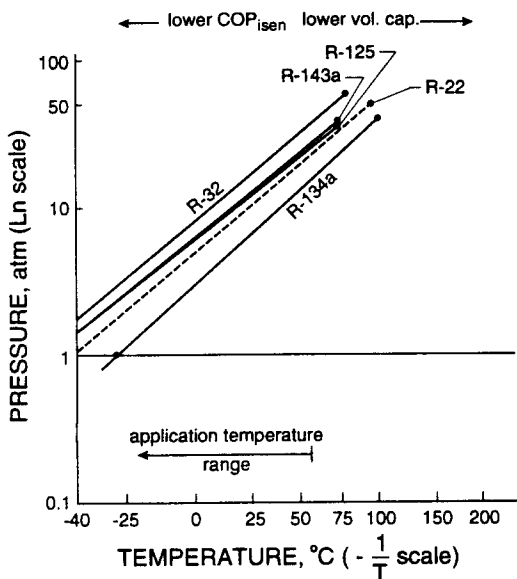


Figure 6. CFC-22 and Mixture Alternatives' Components

On the other hand, HFC-32/125/134a has been designed to have a similar vapor pressure as HCFC-22, so current equipment sizes are immediately available with no need for new product designs (albeit minor modifications may be necessary). It too lends itself to some minor efficiency gains through equipment redesign. The use of counterflow or cross-counterflow heat exchangers to take advantage of temperature glide matching is a possibility (Mulroy, 1988). The larger percentage of more complex molecules (i.e., 100

series refrigerants) in the mixture may also increase the efficiency a point or two through the use of a liquid-line suction-line heat exchanger (Domanski, 1992). Thus, at the present time it is not clear if there will be one or more refrigerant alternatives for HCFC-22. And given the two aforementioned alternatives, it would follow that the new machines could be quite different in size and/or configuration. For this somewhat staid and standardized industry that is used to producing a reliable, efficient, cost-effective product, these design choices offer radical changes indeed. A rather comprehensive summary of the details in the HCFC-22 and CFC-502 alternatives development is presented by Dr. Hickman in the January 1994 ASHRAE Journal.

4. SAFETY: TOXICITY AND FLAMMABILITY

Ever since Thomas Midgley stood on the stage of the American Chemical Society, in 1930, and introduced the first of a new family of refrigerants (CFCs) by inhaling a lung full of what we now call CFC-12 and blew out a candle, the refrigeration industry had its solution to the problem of unsafe working fluids. Over the years, the American Society of Heating, Refrigerating and Air-Conditioning Engineers (ASHRAE) assumed responsibility for maintaining and assigning universal number identifications (see Appendix A) and safety ratings (first column of Tables A1 and A2) for refrigerants. The committees with the safety rating responsibilities are SSPCs 34 and 15, and are now standing committees because of the influx of new refrigerants (ASHRAE Std. 34-1992, ASHRAE Std. 15-1992). The rating

Table 3.
ASHRAE Std. 34 - 1992 Safety Group Classification

	no identified toxicity at concentrations ≤ 400 ppm	evidence of toxicity below 400 ppm	
Higher Flammability	A3 (C_3H_8)	B3	$LFL \leq 0.10$ kg/m^3 or $\Delta H_{comb} \geq 19$ MJ/kg
Lower Flammability	A2 (R-32)	B2 (NH_3)	$LFL > 0.10$ kg/m^3 and $\Delta H_{comb} < 19$ MJ/kg
No Flame Propagation	A1 (R-134a)	B1 (R-123)	
	Lower Toxicity	Higher Toxicity	

group classifications are illustrated in Table 3 along with the

boundary quantifications. An example of one of the more important refrigerants is listed parenthetically in each group; a complete listing is available in ASHRAE Standard 34-1992. Virtually all the CFCs have an A1 rating.

The toxicity groups are divided into two levels—A and B, which are called lower and higher toxicity levels, and represent no toxicity evidence or some toxicity evidence, for a Threshold Limit Value-Time Weighted Average (TLV-TWA) of 400 ppm of refrigerant in air. This type of definition, albeit inclusive of a rigorously defined test procedure, alludes to the recognition that all substances can be toxic, depending on the quantity and the conditions. The determination of the toxicity of new refrigerants has become the responsibility of the Programme for Alternative Fluorocarbon Toxicity Testing (PAFT) which is sponsored by the major producers of refrigerants from nine countries. Each alternative is subjected to over 100 individual toxicity tests over a two to six year period at a cost of \$3-5 million.

Voluminous data has been made available on each of those chemicals now assigned ASHRAE numbers. A summary of the more significant data and conclusions on the two most currently important alternatives (i.e., HFC-134a and HCFC-123) are presented in the July 1994 ASHRAE Journal (Calm). The summarization of this summary article, for HFC-134a at least, might be done in one sentence:

"Based on current toxicity findings, R-134a is regarded as one of the safest refrigerants yet introduced."

Unfortunately, the same cannot be said for HCFC-123, which has led to considerable bad press and in some cases exaggerated negative marketing practices. Whereas most refrigerant manufacturers recommend the TWA exposure not to exceed 1,000 ppm for HFC-134a, they limit HCFC-123 to 10 to 30 ppm. However, this limit is still an order of magnitude greater than the .67 ppm of refrigerant that is likely to exist in a properly maintained machine room, even during refrigerant transfer activities. Or as stated in Calm's article:

"A more instructive comparison is between the alternative refrigerants and those they replace."

Contrasting R-123 with R-11 shows the alternative refrigerant to be much safer in many respects, particularly for acute toxicity indicators. The lethal concentration by inhalation is nearly 25% higher; the cardiac sensitization level is four times as high. The recommended exposure limit for chronic (long-term, repetitive, or sustained) exposures is much lower, however.

The chronic exposure limit for R-123 is more than 15 times higher than the maximum concentration measured in machinery rooms—based on two independent studies of 17 plant—provided that recommended installation, handling, and service

procedures are followed (Meridian Research 1991, Trane 1991). The 30 ppm limit recommended by two chemical manufacturers is 45 times higher."

At this time, the toxicity rating of mixtures is based on the mass weighted average of the components.

As with toxicity, the flammability rating of refrigerants is at the same time vague and rigorous. Well defined laboratory test apparatus and conditions exist but what constitutes flammability and how well the lab test represents field situations is eternally debatable. Nevertheless, the need for ratings are paramount for liability, etc. and so the best that experts have to offer is currently being utilized but continually reevaluated.

The flammability categories are based on the ASTM E681-85 test for establishing the lower flammability limit (LFL) and the calculation of the heat of combustion as described in ASHRAE Standard 34 of the refrigerant. Three groups: 1, 2, and 3 represent no, lower, higher flammability under 25°C refrigerant/air temperature conditions with a match ignition source. Groups 2 and 3 are mostly populated by halogens and hydrocarbons, respectively, with ammonia at the upper end of Group 2 (i.e., $\Delta H = 19000$ kJ/kg).

Following in the tradition of the industry, since the 1930's, all the new refrigerants (i.e., halogens) that are of a single component, are simply not flammable under any reasonable conditions they may encounter either in a system or in storage. At least, that is what the Group 1 rating is attempting to imply. Of course, this is the refrigerant only rating procedure and does not cover the fact that flammable lubricant may also atomize out with the refrigerant from an uncontrolled system leak.

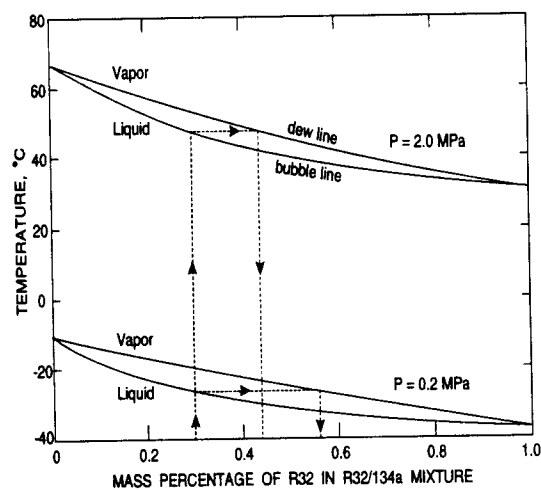


Figure 7. Phase Diagram of HFC-32/134a Zeotrope

All the mixtures (as formulated) that have been proposed to ASHRAE, so far, are non-flammable. However, the mixture rating procedure is complicated by the need for a

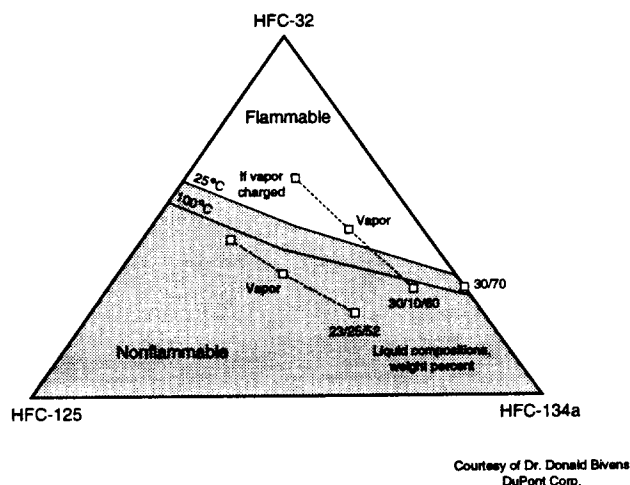


Figure 8. Flammability Regimes of HFC-32/125/134a

second rating (worst case fractionation) for both azeotropes and zeotropes. The mixture phase diagram in Figure 7 illustrates the problem. Consider a system that was liquid charged with the simple binary HFC-32/134a, formulated with a weight composition of 30%/70%, respectively. The flammable component HFC-32 is the more volatile so while in the liquid phase there exists 30% in the vapor phase at condenser pressure of 2.0 MPa, a vapor leak would have about 42% HFC-32; still nonflammable. However, the same system would leak HFC-32 vapor from a 0.2 MPa evaporator in the high 50 percentile range, a range which is flammable. The ASHRAE committee 34 requires measured data for worst case fractionation at -40°C and flammability test at 25°C. However, there is a strong movement towards increasing the 25°C to 100°C because Underwriters Laboratory (UL) has recently reaffirmed that they would continue to require such. As can be seen in Table A1 one zeotropic mixture's worst case fractionation caused the rating to be in the lower flammability region (i.e., Group 2).

ASHRAE and UL both recognize that in spite of expected training about the need to liquid charge zeotropes into a system, so as to maintain the "as formulated" composition that exists in the shipping container, sometimes vapor charging will occur. Therefore, they are considering requesting measured fractionation and flammability tests of compositions that would result from such an occurrence.

Figure 8 represents the ternary HFC-32/125/134a phase diagram of two different "as-formulated" compositions 30/10/60% mass and 23/25/52% mass. These liquid compositions are both nonflammable but the equilibrium vapor state associated with each is in the first case flammable and the second nonflammable. It was this phenomena that determined that the 23/25/52 composition would be marketed in spite of the fact that the 30/10/60 fluid has a higher thermodynamic performance. If, however, vapor charging from the shipping container into the refrigeration system was conducted the composition of the system liquid would be that of the shipping container's vapor and the system's vapor composition would be even more dominated

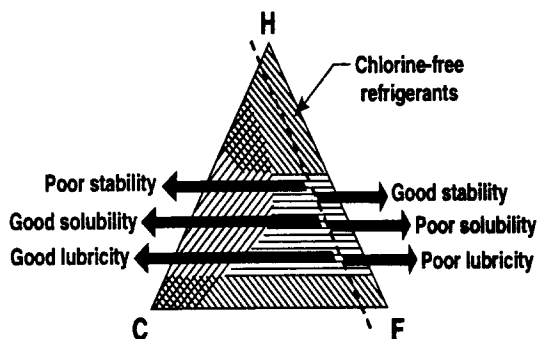
by the more volatile components HFCs-32 and 125, as indicated. In this case, because the HFC-32 is flammable, the composition moves closer to the flammable region but still not into it. Also, noted on the ternary diagram is the binary HFC-32/134a at the controversial 30/70% mass composition. Whether its liquid is flammable or not depends on conditions (e.g., refrigerant/air temperature) at which the test was conducted. Such differences have led the Japanese to continue to consider the binary (even though the vapor would test flammable at reasonable fractionation temperatures) as an alternative and the Americans adding the HFC-125 (at a cost in efficiency) to be more safety conservative.

A summary of the flammability limits, both lower and higher, of the various alternatives is presented in the reference by Richard 1992.

As implied earlier, all chemical fluids are unsafe (i.e., toxic or flammable) under certain conditions. Laboratory tests do not simulate field conditions, precisely. No one can conceive all of the possible scenarios that can occur in the field; particularly if proper maintenance and operational procedures are not heeded. Therefore, all that can be done is to set up a series of tests which will appear to give a reasonable assurance that the alternatives are safe when used properly. In the case of zeotropes, it is obvious that new comprehensive field training of maintenance personnel will be required.

5. MATERIALS COMPATIBILITY

The fact that air conditioning and refrigeration machinery typically has a life of 20 to 30 years is, in large part, due to the various materials (i.e., refrigerants, lubricant, metals, polymers, etc.) maintaining functional properties over time. This compatibility is somewhat surprising when one thinks about how many millions of temperature cycles are imposed on the two fluids, refrigerant and lubricant, which are in intimate contact with virtually all interior materials. The relationship between the refrigerant and lubricant is, of course, most important. The effects on this relationship, by



Courtesy of Dr. Hans Spauschus

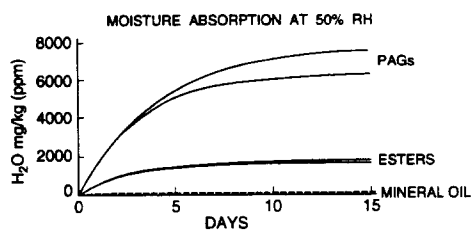
Figure 9. Prediction of properties of Refrigerants with Mineral Oils

eliminating the chlorine from the refrigerant, is illustrated in Figure 9 for the traditional mineral oils, including the synthetic alkylbenzene. Figure 9 is similar to Figure 2 in that the chlorine-free refrigerants are to the far right side of the triangle, where their interaction with the lubricant is to improve stability but decrease solubility and lubricity. It is the latter consequences that made the traditional oils unacceptable and a simultaneous hunt for new lubricants began almost the same time as that for refrigerant alternatives. The first family to emerge was polyalkylene glycols (PAGs). The automotive industry quickly adopted these for vehicular air conditioning and have developed system compatibility to a state that many automobiles systems are now commercially available. Even field studies about retrofitting are being reported with much success (Automotive Engineering, 1994).

The stationary systems industry, with its demands of longer life (i.e., hours of operation) and often lower temperatures, was not as satisfied with PAGs because of possible interactions between PAGs and residual chlorine from solvents used in the manufacturing process. Although the chemical stability of PAG/HFC was superior to that of mineral oils with CFCs or HCFCs, water absorption was considerably higher and hydrolytic stability was lower. Thus, a second family of lubricants, known as polyolesters (POEs), was developed. (Actually POE lubricants have been used in aircraft engines for 20 years. From these, higher viscosity grades with improved resistance to hydrolysis were developed for air conditioning and refrigeration applications.) A more quantitative summary of these property effects is presented by Spauschus 1991 from which Figure 10 in this paper has been

taken. The reduction in water absorption by the POEs, relative to the PAG's, has been a major factor in the rapid adoption of this family of lubricants. The fact that POE's water absorption level is still higher than the mineral oil/CFC level the machinery systems are used to, suggests a need to obtain specific advice about the proper filter/dryer for a specific POE/HFC pair. Since "free water" has the potential to break down the POEs into acid and alcohol one should purchase the highest quality lubricant with the best hydrolytic stability for long machine life (Spauschus, 1994). Also important to note, is that the absorption takes place over a period of days, therefore, care should be taken during the storage and transferring stages so as not to expose the lubricant to the air more than necessary.

CFC-12 MINERAL OIL 10-20 PPM (Nominal)	HFC-134a/ESTER PPM (Nominal) 50-100 "Dry" 100-300 "Wet"	HFC-134a/PAG PPM (Nominal) 50-200 "Dry" 200-1200 "Wet"
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Courtesy of Dr. Hans Spauschus
Spauschus Associates

Figure 10. Moisture Absorption by Lubricants

Lubricants have always been somewhat enigmatic to machine owners and operators because of the many proprietary additives. The same is true for the new lubricants and it, therefore, will be very important to follow the advice of both the refrigerant and compressor manufacturers as to which and how much specific lubricant should be used for a specific system and application. This is particularly important for retrofit sites where flushing specifications for the old refrigerants and lubricants are needed. Compressor manufacturers rely on the lubricant/refrigerant mixture to perform in different ways to ensure that sufficient lubricant exists at each critical point at all times. Such qualities as "misting", "controlled foaming", ability to withstand "squeezed film", "splash", etc., etc., are desirable. Different compressor designs may require one or more of these qualities to lubricate one or more of the critical bearing areas. The only method for ensuring satisfactory performance is extensive laboratory and system testing. At this time, it is safe to say that all manufacturers are not completely satisfied with HFC/POE mixtures in all their compressors. Therefore, the door for yet another lubricant family remains open. However, solutions to current problems may lie with the use of lubricant additives and/or compressor design changes. Considering the development time already invested, it is likely that the ester family lubricants, in some form, will prevail in use with HFC refrigerants.

Several studies of retrofitting CFC-12/mineral oil

systems which service refrigeration shipping containers (Heap, 1993 and Fleck, 1993) and walk-in boxes (Shaw et.al., 1993) have recorded the lubricant exchange procedure and effects on materials. In general, the lubricant exchange procedure's goal was to reduce the amount of residual mineral oil to less than 1%. This was usually achieved by two or three flushings; that is draining the existing lubricant and replacing it with a full charge of the appropriate POE. Between each draining the system was operated for several hours to a couple of days with its usual CFC-12 charge. After the 1% mineral oil level was attained the new HFC-134a/POE charge was implemented. In virtually all cases, satisfactory lubrication performance was experienced for the length of the tests. Some materials problems were experienced, however. In particular, it was essential to use gasket, seal, and sump plug materials that have proven to be compatible with a HFC-134a/POE liquid mixture. Finally, it should be noted that, to date, most of the research with POEs/HFCs has been associated with HFC-134a. Although these conclusions should generally be applicable to other HFCs, mixtures containing HFC-143a and particularly HFC-32 may be more troublesome because of their high molar polarity. One should be careful that specific tests with these specific refrigerants have been conducted before using them.

A formal research program under the direction of the Air Conditioning and Refrigeration Technology Institute, which is related to the Industry's trade association, and the sponsorship of the U.S. Department of Energy has been conducting such a variety of tests since 1991. These are summarized by the following general conclusions (Ernst 1993):

- *Materials currently used for hermetic motors are at least as compatible with R-32, R-125, R-134a and R-143a and polyolester lubricants as with R-22 and mineral oil.*
- *Commercial elastomer materials are available that are compatible with R-32, R-125, R-134a, and R-143a and polyolester lubricants. Most elastomers were affected more by R-22 than by alternatives.*
- *In general, HFC's had less effect (on plastics) than HCFCs. However, Acrylonitrile-Butadiene-Styrene terpolymer, polyphenylene oxide, and polycarbonate plastics were incompatible with most alternative refrigerants.*
- *R-32, R-125, R-134a, and R-143a with polyolester lubricant had excellent stability at temperatures to 160°C after 14 days, similar to R-22 with mineral oil. In tests at 200°C polyolester and polyglycol lubricants exhibited increased acid numbers as a result of some decomposition.*
- *R-32 and R-134a are widely miscible with polyolester lubricants. R-125 is less miscible and R-143a has large immiscible regions. This data suggests that the blend (mixture) alternatives for*

R-22 and R-502 may be less miscible with polyolester lubricants compared to R-22 and R-502 and mineral oils.

Several studies are continuing which will contribute to an ever expanding data base. As a result, the ARTI/DOE program also sponsors a computerized data base of abstracts of these and other studies contributed by the Industry. It is available along with quarterly updates from Calm's Refrigerant Database.

6. THE CFC-114 ALTERNATIVES

Given all the variables, problems and opportunities discussed, there can be little doubt that the owner/operator of a major refrigeration/air conditioning systems is going to have difficult decisions to make as to whether to retrofit or buy new. Further choices may be necessary as to which alternative or alternative system the conversion should assume. CFC-114 replacement makes an interesting example because it is primarily used in to marine applications and it has several alternatives.

Figure 11 illustrates the vapor pressure of CFC-114 along with some alternatives. The CFC-114 vapor pressure lies between, but far enough away from, HFC-134a and HCFC-123 that major machine design changes would be required and retrofitting would probably not be economical. In any case, retrofit or new, HCFC-123 would be unacceptable for sea duty for the same reason CFC-11 has been, that of sub-atmospheric evaporator pressure. HFC-134a has a vapor pressure significantly higher than CFC-114 and when one considers that the ASME pressure vessel code requires a system to be designed to hold five times the condenser pressure, it may be doubtful that many existing CFC-114 systems could meet the 1.0165 MPa (10 atm.) requirement. A small efficiency penalty would almost surely occur, at least in theory, but the HFC-134a alternative for a new system remains a viable candidate. Inherently, the machinery should be a somewhat smaller system due to the refrigerant's higher volumetric capacity. Furthermore, it is beginning to be widely used in the commercial field and, therefore, is a "safe bet" for solid support and future machinery developmental improvements.

For the purposes of retrofitting CFC-114 systems, HCFC-124 has possibilities in spite of its political life of only another decade or so. As can be seen from Figure 11, its vapor pressure is much closer to that of CFC-114 than any of the other refrigerant alternatives that are now commercially available. The pressure differences, between CFC-114 and HCFC-124, seem to have some consequences however. The lower critical temperature suggests that the HCFC-124's theoretical efficiency will be lower, but its increased latent heat (i.e., refrigeration effect) compensates and the ideal cycle efficiency of both fluids appear to be quite similar. But its different thermodynamic properties will require a smaller centrifugal compressor of higher speed and, thus, higher windage losses. The high pressure will also require that the CFC-114 pressure vessels be analyzed for structural integrity. Also, higher bearing pressures can be expected so there is

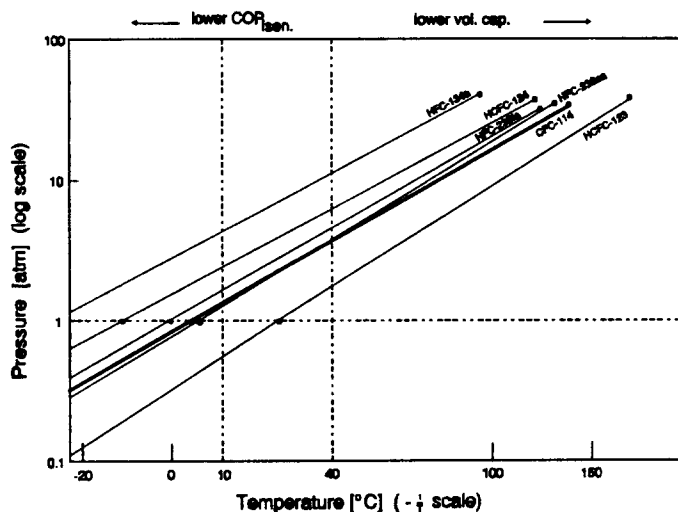


Figure 11. Phase Diagram of CFC-114 Alternatives

little in the compressor conversion that would indicate anything other than lower compression efficiency (Hickman, 1994). Of course, it is always possible that heat exchanger performance or other components will make up for some of these negative consequences but it shouldn't be surprising that by putting a refrigerant into a system which was originally designed for something else, the system would perform less effectively. Just how much less effective will be an important piece of information for the equation to determine whether one should retrofit or replace.

HFC alternatives have also been considered as possible replacements for CFC-114. The ones that have emerged as leaders are two isomers (i.e., ea and fa) of the partially fluorinated propane molecule, HFC-236. Figure 11 illustrates one of their more attractive attributes in that their vapor pressure is quite similar to CFC-114; so that the new system component designs should be of similar size. Several EPA studies have quantified the merits of HFC-236ea (Smith, 1993 and Kazachki, 1993). If for some reason the HFC-236ea is not satisfactory, the symmetrical molecule HFC-236fa may be a candidate retrofit fluid. Neither of these isomers have been mass produced so commercial costs are not available, but it is generally considered that symmetrical molecules are more difficult and thus more expensive to manufacture. The HFC-236fa vapor pressure difference from CFC-114 appears small enough to use an existing compressor design albeit a different size. All of these fluids, because of their high heat capacity, would likely increase in efficiency if expansion side equipment, such as liquid line/suction line heat exchangers or economizer cycle were incorporated within the system (Domanski, 1992). But, of course, this would have to be verified with actual equipment. However, considerable verification of compatibility and safety properties plus full system tests may not be completed in time for a commitment as a *transitional period alternative* even if early optimistic reports hold true. Since new alternative machines are likely to go through developmental stages for some years to come, there would appear to be some benefits in staying with equipment

which will be used in the much larger commercial market.

7. CONSEQUENCES

This paper has attempted to describe the impact on system performance and operation resulting from the elimination of chlorine from refrigerants; that is from CFCs to HCFCs to HFCs. The CFCs started to become available over 60 years ago. No new refrigerants have emerged in several decades. It has been known for at least that long that simple molecules provide the best thermodynamic performance (operating costs) while requiring the lowest capital costs. The chlorine provided a strong link with the solubility and lubricity of the oil and metal surfaces (reliability). The building codes, machine room and handling specifications are based on the assumptions that refrigerants are nontoxic and nonflammable (safety). All of this has been upset by the need to protect the environment. It is possible to do this but a price will be paid—very likely in capital costs. Also, it will take time and mistakes are inevitable. The transition period will force owner/operators to make difficult purchasing decisions—retrofit or buy new. Training about new lubricants, mixtures handling, equipment "tightening", new service practices, emissions reduction, etc., will be mandatory. There is no substitute for the education that each person in this field must now acquire if he or she is to remain competent. Never before have the chemical and equipment manufacturers cooperated so successfully in the R&D efforts as in the development of the new refrigerants and lubricants in relation to thermophysical properties, safety issues, heat transfer data, compressor calibrations, etc., and they have made considerable information available to the public which is of a highly professional nature. But as individual products are developed for marketing, the competition will again dominate and purchasing decisions will again be filled with pros and cons based on sales literature. Thus, a continual updating on the technical developments will be a personal responsibility for years to come.

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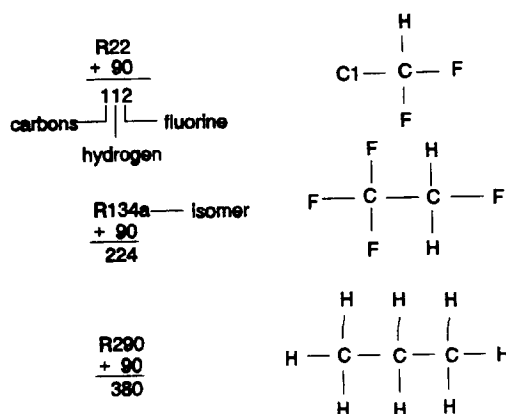
Appendix A:

Refrigerant Numbering System

<u>000's</u>	Methane Series
<u>100's</u>	Ethane Series
<u>200's</u>	Propane Series
<u>300's</u>	Cyclic Organic Compounds

Ref. No. + 90 = carbon atoms/hydrogen atoms/fluorine atoms openings filled with chlorine atom unless suffixed for bromine content.

Examples: (for above series, only)



<u>400's</u>	Zeotropic Mixtures in order of granting safety classification
<u>500's</u>	Azeotropic Mixtures in order of granting safety classification
<u>600's</u>	Miscellaneous organic compounds each decade: hydrocarbons oxygen compounds sulfur compounds nitrogen compounds
<u>700's</u>	Miscellaneous inorganic compounds (and 7000's) 700+ molecular weight example: ammonia 717
1000 thru <u>1200</u>	Unsaturated organic compounds

Table A1. Alternative Mixtures containing HCFCs

ASHRAE No. (Rating)	Composition (% weight)	temp. glide (°C) @ atmos. press.	replacement for	brand name
401 A (A1/A1)	R-22/152a/124 (53/13/34)	4.9	CFC-12	MP 39
401 B (A1/A1)	(61/11/28)	4.6	CFC-12	MP 66
401 C (A1/A1)	(33/15/52)	4.7	CFC-12	MP 52
402 A (A1/A1)	R-125/290/22 (60/2/38)	0.9	CFC-502	HP 80
402 B (A1/A1)	(38/2/60)	1.0	CFC-502	HP 81
403 A (A1/A1)	R-290/22/218 (5/75/20)	2.5	CFC-502	ISCEON 69S
403 B (A1/A1)	(5/56/39)	0.9	CFC-502	ISCEON 69L
405 A (A1/A1)	R-22/152a/142b/C318 (45/7/5.5/42.5)	5.6	CFC-12	G2015
406 A (A1/A2)	R-22/600a/142b (55/4/41)	9.9	CFC-12	GHG
*408 A (A1/A1)	R-125/143a/22 (7/46/47)	0.5	CFC-502	FX 10
*409 A (A1/A1)	R-22/124/142b (60/25/15)	7.9	CFC-12	FX 56

Table A2. Chlorine-Free Mixture Alternatives

ASHRAE No. (Rating)	Composition (% weight)	temp. glide (°C) [†] @ atmos. press.	replacement for	brand name ^{††}
404 A (A1/A1)	R-125/143a/134a (44/52/4)	0.8	CFC-502	HP 62, FX 70
407 A (A1/A1)	R-32/125/134a (20/40/40)	6.4	CFC-502	KLEA 60
407 B (A1/A1)	(10/70/20)	4.1	CFC-12, CFC-502	KLEA 61
*407 C (A1/A1)	(23/25/52)	7.1	HCFC-22	AC9000, KLEA 66
	(30/10/60)	7.4	HCFC-22	
	R-32/125/143a (10/45/45)	0.5	CFC-502	FX 40
	R-32/134a (30/70)	7.4	HCFC-22	
507 (A1)	**R-125/143a (50/50)	0.0	CFC-502	AZ 50
*410 A (A1/A1)	R-32/125 (50/50)	<0.1	HCFC-22	AZ 20
*411 A (A1/A2)	R-1270/22/152a (1.5/87.5/11)	?	HCFC-22	G2018A
*411 B (A1/A2)	(3/94/3)	?	CFC-502	G2018B
	R-290/600a (50/50) varies	8.6	CFC-12	OZ 12
<p>* Approved by ASHRAE committee SSPC 34 for public review, comments invited.</p> <p>** Azeotrope exists for low evaporator temperatures.</p> <p>[†]Temperature glide = $T_{\text{dew}} - T_{\text{bub}}$, as predicted by REFPROP 4.0 (Actual temperature glide about 15% less for evaporators)</p> <p>^{††}<u>Manufacturers:</u> DuPont - MP, HP, AC ATOCHEM - FX G - Greencool Allied - AZ Rhone-Poulenc - ISCEON GHG - Monroe Air Tech ICI - KLEA Foron - OZ</p>				

Appendix B:

Ammonia

Ammonia is certainly one of the oldest and best understood refrigerants known. Its thermodynamic properties (e.g., high latent heat, high critical point, low liquid heat capacity) support its inherent high efficiency in the ideal vapor compression cycle. Years of use in a wide variety of applications have established a solid foundation for most system and application designs. On a performance basis, it is clearly competitive if not superior to most halogenated refrigerants. On an economic basis, the alternative refrigerants cost is approaching an order of magnitude increase over CFC's and as much as 50 times that of ammonia. However, ammonia's limitations show up in the materials compatibility and safety areas.

The highly corrosive nature of ammonia, with copper, zinc, and their alloys, makes these materials unavailable. One of the ramifications of this limitation is that it is not likely that ammonia will be adopted for small unitary systems. First of all, with the various mixtures becoming available the need for ammonia is not that great. Then with the elimination of hermetic compressor/motor systems, soldered pipe connections, and the enhanced heat transfer surfaces available in copper tubes (Starnes, 1993), it is unlikely that a small ammonia system will be developed, so that it could compete either economically or performance-wise with halocarbon systems (Pilllis, 1993).

In larger systems ammonia becomes more performance competitive but still has limitations. Most safety codes would prevent the use of DX coils in ammonia systems so air conditioning applications would be likely only where package water chillers make sense anyway. With plate heat exchangers becoming more cost effective and available in non-copper materials, several new packaged chillers have become available in the 6 to 350 tons (20 to 1200 kW) range. At least one of these uses a semi-hermetic motor; implying that as R-22 is phased out motor shielding development may eventually allow for ammonia cooling (Pilllis, 1993). Typically, these systems also have supplemental compressor cooling (except for oil flooded screws where cooling occurs within the compressor) because of the high discharge temperature inherent to ammonia's simple light weight molecule.

In large field erected refrigeration systems ammonia has always been widely used and with the eventual elimination of its main competitor, R-22, there is little reason to think that this will not continue. In fact, with the current R-22 alternatives being zeotropic mixtures, which are particularly troublesome to use in flooded evaporator systems (due to potential composition shift with load), the ammonia usage in this area may well expand. In these systems hermetic motor/compressors and copper tubes and heat exchangers are not used anyway. Also, the large charge requirements make ammonia costs attractive. Thus, as Pilllis states, "Ammonia is already the refrigerant of choice in large refrigeration applications for the previously-mentioned reasons. The only limitations to its use are code restrictions that become too costly to meet".

These code restrictions are concerned primarily with ammonia's toxicity and flammability. Voluminous documents

have written on this subject and the degree to which restrictions apply are closely aligned with application. Stera (1993) outlines the requirements listed in the Lloyd's Register document "Guidance Notes for Ammonia Marine Plant". He states that the objective of these notes are prevention of leakage and the containment and safe disposal of ammonia from the plant. He further states that "The ammonia will only be accepted in the indirect refrigeration system incorporating a secondary refrigerant, such as brine". This, of course, will limit the size of a single ship-board ammonia plant to that which can be packaged.